INFLUENCE OF REFERENCE ELECTRODE POWDER CHARACTERISTICS ON PERFORMANCE OF ZIRCONIA OXYGEN SENSORS

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Reference electrode powder is an important part, which affect performance of zirconia oxygen sensors. The new reference electrode powders with variations in terms of Cr_2O_3–Fe_2O_3 composition and chromium-oxide ratio have been produced by chemical coprecipitation method. The microstructural characterization of the reference electrode powders were conducted using scanning electron microscopy (SEM). Performance of the reference electrode powders was tested in oxygen activity measurements at molten steel under industrial steelmaking practice. The powders produced by the oxide coprecipitation work very well in terms of the EMF reproducibility and of the response time for the low oxygen content measurements. The chemically produced Cr_2O_3–Fe_2O_3 powder mixtures very well attach to the Cr particles. This fact gives good electromotive force (EMF) reproducibility with accurate Al response. Elevated Fe_2O_3 content of the oxide powder reduces the EMF overshoot and improves the measurement accuracy. More positive EMF measurements, lower Al predictions than the chemical analysis and reduced probe accuracy at higher Al contents are obtained with decreasing the oxide content of the reference powder.

INTRODUCTION

The control of oxygen content in molten steel is one of the critical importance in steelmaking from stand point of proper deoxidation, steel cleanliness, good recovery of alloying additives and final product quality. In order to control the oxygen content in the steel, the knowledge of the oxygen concentrations or activities at various stages in the process is required. This can be directly achieved by using an oxygen sensor [1-3]. The oxygen sensor is an indispensable tool for process control in steelmaking, such as the estimation of carbon content at blow end of basic oxygen furnaces, or improvement in aluminum control in the secondary refinement [4,5]. The oxygen sensors are today regularly used in the areas of converter steelmaking, ladle treatment and casting of the steel [6].

The oxygen sensor is a simple oxygen concentration cell, which is mainly composed of a solid electrolyte and a reference electrode. Magnesia-partially stabilized zirconia (Mg-PSZ) having ionic conductivity at higher temperatures is widely used as the solid electrolyte in the form of a closed end tube [7-9]. The oxygen reference electrode in the cell is powder mixture of metal and its oxide. The sole purpose of the reference material is to ensure that the activity on one side of the solid electrolyte remains constant. For this purpose, a metal-metal oxide system is used which, at a known temperature, gives a fixed oxygen activity. A powder mixture of $Cr–Cr_2O_3$ is the best known reference material for the oxygen sensors due to its oxygen activity very close to the that of the molten steel [10,11].

In industrial applications, the accuracy and the reproducibility of the oxygen measurements and success rates are satisfactory, in general [12]. However, the oxygen sensor is still capable of further improvements from the viewpoints of the solid electrolyte and the reference electrode. The response time of the sensor in oxygen content less than 10 ppm, as observed after deoxidation processes, needs to be improved. Since the EMF of the sensor takes a longer time to stabilize in such a low range, immersion process of the sensor into molten steel takes longer time until the oxygen cell reaches its equilibrium state. Mochizuki and co-workers [13] reported that the zirconia tube with a thinner tip end thickness and less amount of $Cr–Cr_2O_3$ powder reduces the response time of the cell. Worrell and co-workers [14] developed an extended-life oxygen sensor for the iron and the steel melts using isostatic fabrication technique. On the other hand, Dimitrov and co-workers [15] studied new oxygen reference materials, which exhibit lower oxygen partial pressures than that of $Cr–Cr_2O_3$ to reduce gradient of the oxygen potential for semi-killed or fully killed steels.

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The aim of the present investigation is to understand the influence of new reference electrode powders on the performance of the commercial sensors in terms of EMF reproducibility, the response time and the accuracy in soluble Al predictions. The study is concerned with chemically produced powders and their characteristics including variations in the oxide composition and the metal/metal oxide ratio.

EXPERIMENTAL

The reference electrode powders given in table 1 were produced by chemically oxide coprecipitation method [16]. The powders varied in terms of Cr_2O_3–Fe_2O_3 composition, and chromium-oxide ratio. In order to prepare the oxide part of the powders, raw materials used were reagent grade $Cr(NO_3)_3.9H_2O$ and $Fe(NO_3)_3.9H_2O$. The nitrate salts were dissolved in distilled water individually, then mixed corresponding to the compositions and stirred simultaneously. The mixture was hydrolyzed by pouring aqueous ammonia, while pH value was maintained at 7. The precipitates were washed several times and then the required amount of hydroxide/water sediment was mixed as slurry with coarse Cr particles around 100 μm in size. The mixture obtained was dried at 100°C for 24 h and finally calcined at 700°C for 2 h.

The chemically produced powders around 30 mg were injected into the commercial Mg-PSZ tubes and back-filled with fine alumina powder. The oxygen cells were then mounted into modules and sand-filled by a domestic supplier. Figure 1 shows structure of the test probes. The main elements of the cell (figure 1a) are a Mg-PSZ solid electrolyte (A), a chemically produced reference electrode powder (B) and a Mo lead wire (C), as shown on SEM micrograph (figure 1b). The oxygen sensors were finally dipped into the molten steel, together with the commercial probes containing standard powders (CP) and samples for chemical analysis (Lab). The industrial trials were repeatedly conducted in low oxygen content on a degasser of secondary metallurgy under industrial steelmaking practice. Each oxygen sensor was applied for one quick EMF reading only. The performance of the reference powders was summarized in terms of mean difference (X), standard deviation (S) and response time, according to number of the test probes (N).

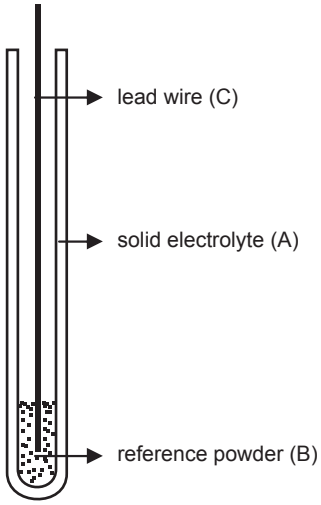
Table 1. The reference powders produced by oxide coprecipitation method.

Reference powder	Composition (wt.%)	Chromium/oxide ratio (%)
RP15a	85 Cr_2O_3/15 Fe_2O_3	90/10
RP15b	85 Cr_2O_3/15 Fe_2O_3	95/5
RP25a	75 Cr_2O_3/25 Fe_2O_3	90/10
RP25b	75 Cr_2O_3/25 Fe_2O_3	95/5

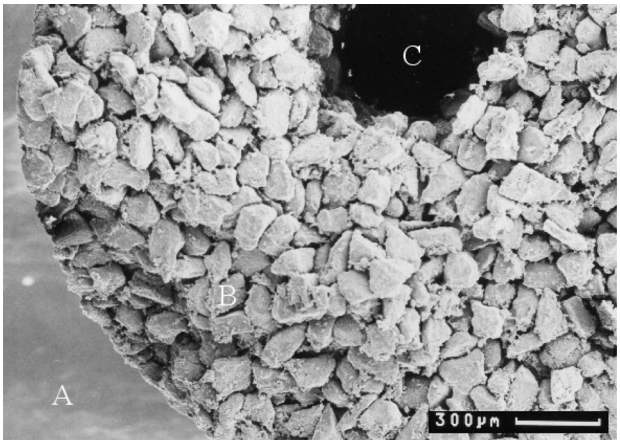
The oxygen sensor structure and the powder morphology after the calcination and the immersion to the molten steel were examined using JEOL JSM 5400 SEM.

RESULTS AND DISCUSSION

Examination of the coprecipitated powders by SEM revealed that the powder particles were very fine and homogeneous in size. Figure 2 shows typical SEM image of the reference powder. The fine oxide powders adhere very well on the coarse Cr particles (figure 2a). In a higher magnification (figure 2b), it is clear that the particle size are generally less than 2 μm in size. Thus, the coprecipitation method produces very fine spherical particles of Cr_2O_3–Fe_2O_3 having large surface area for ionic bonding between chromium and oxide mixture. Due to smaller particles and hence, higher surface area for reaction, production of the oxides by the coprecipi-



a)



b)

Figure 1. Structure of the test sensors: (a) schematic; (b) cross-section.

tation method might give higher EMF reproducibility and faster response times during the oxygen activity measurements in the molten steel.

The immersion tests were conducted using the oxygen sensors with the chemically produced powders having two different compositions for the investigation of the influence on the sensor performance. The sensor parameters such as temperature (T), EMF and oxygen concentration of the steel bath (a_o) were measured during the immersion tests and several results obtained are given in table 2. In general, the oxygen concentration of the steel bath was lower than 10 ppm, which could introduce errors in the measurements due to the polarization effects [17].

Table 2. The oxygen sensor parameters measured in the performance tests.

Trial	Powder	T (°C)	EMF (mV)	a_o (ppm)
1	RP15a	1566	-120	5.02
	RP25a	1562	-122	4.75
	CP	1570	-126	4.82
2	RP15a	1591	-109	6.95
	RP25a	1591	-111	6.77
	CP	1592	-109	7.00
3	RP15a	1580	-159	3.25
	RP25a	1580	-157	3.34
	CP	1582	-156	3.40

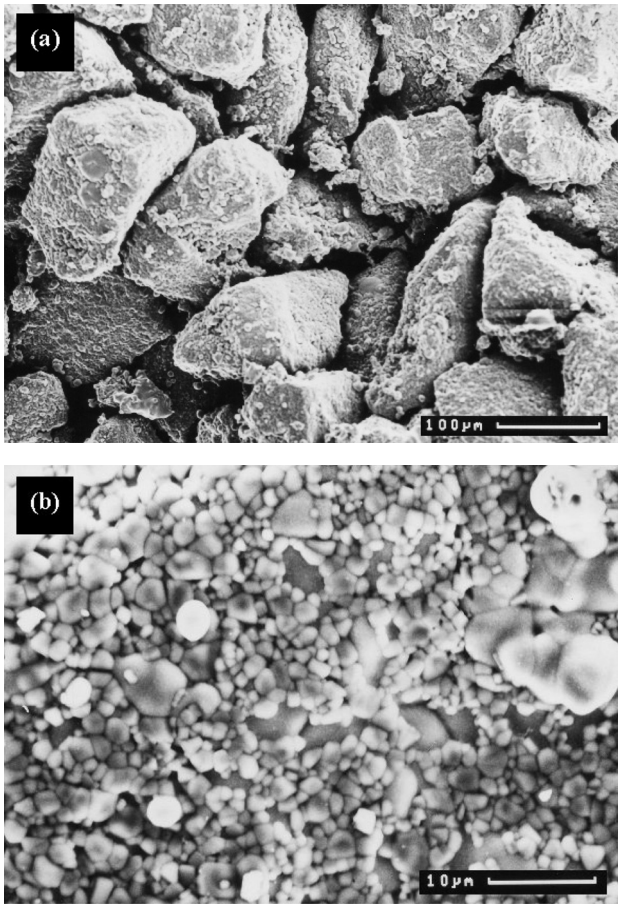


Figure 2. SEM micrographs of RP15a powder: (a) low magnification; (b) high magnification.

In addition, the probe performance was tested in term of Al content predictions. In the production of Al-killed steel indicating low oxygen content, close control of the aluminum content in the molten steel is required to obtain the desired grain size of the final product [18]. The results are shown in figure 3. The coprecipitated powder RP15a brings reproducible values, while the mean difference and the standard deviation in predicted Al contents were 0.0018 and 0.0041, respectively (figure 3a). Reproducible results were obtained also with probes containing the RP25a powder (figure 3b) and CP powders (figure 3c), which were tested as a reference.

The chemically produced powders have good performance against aluminum content obtained by the chemical analysis. However, examination of the EMF traces indicates that RP25a composition tends to give a slightly flatter trace. According to the trial results, it has been found that increasing Fe_2O_3 content in the reference oxide system reduces EMF overshoot and improves the trace quality. The RP25a powder exhibited a small overshoot of about 2 mV, while the overshoot was around 6 mV for RP15a powder.

The response time traces for RP15a, RP25a and CP powders are shown in figure 4. The chemically produced powders gave the response times very close to each other and to the commercial ones. The reproducibility in the response times is very consistent for all chemically produced powders. The thermal equilibrium time was below 5 seconds. These results ensure that the new reference powders are feasible with the stable EMF readings for the industrial applications.

From the literature, it is believed that 10% oxide content in the reference electrode powder gives a close relationship to the chemical analysis results [15]. In this study, the oxygen probes were tested with the chemical production powders having different Cr/oxide ratio such as 90/10 (RP15b) and 95/5 (RP25b) proportions, in weight. Figure 5 shows the results of the Al predictions. The results indicated that the EMF measurements became more positive and the Al predictions were lower than those from the chemical analysis with lower oxide content in the reference powder mixture. However, the EMF reproducibility increased, presumably due to more repeatable oxide content within each individual probe. On the other hand, the Al-mV scale became more compressed giving reduced probe accuracy at higher Al contents, when decreasing the oxide content of the reference powder.

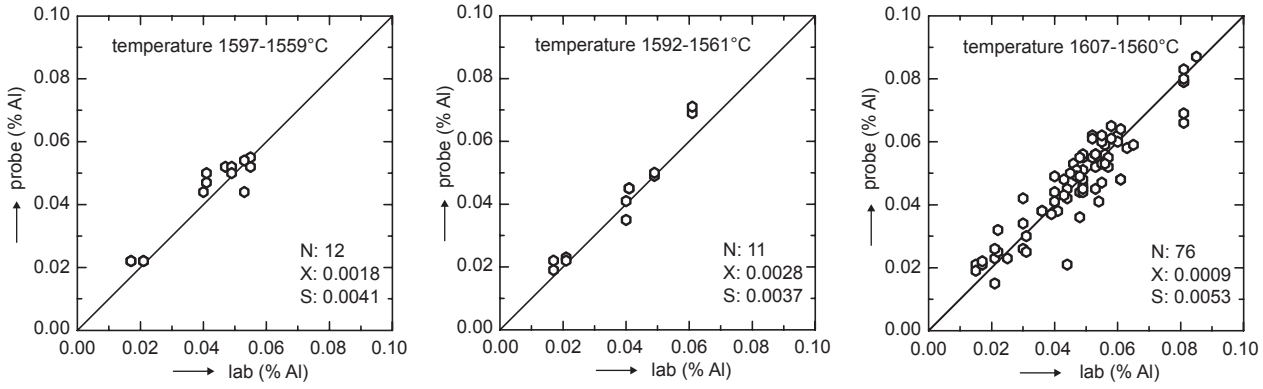


Figure 3. The performance of the reference powders used in the measurements of the low oxygen content: (a) RP15a; (b) RP25a; (c) CP.

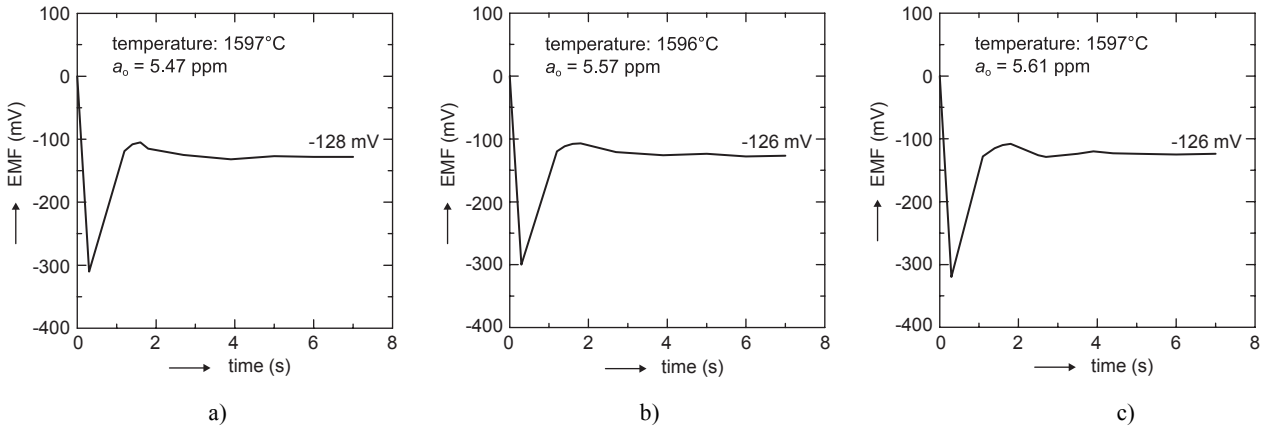


Figure 4. The response time traces of the reference powders: (a) RP15a; (b) RP25a; (c) CP.

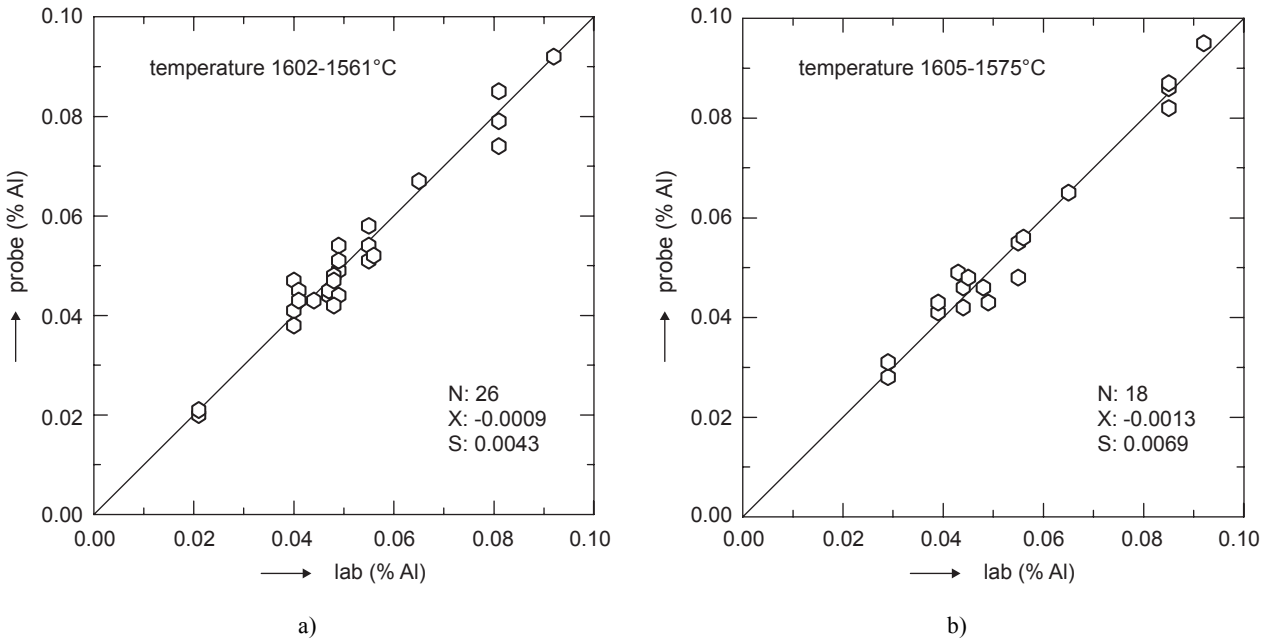


Figure 5. Influence of the chromium-oxide ratio of the reference powders on the sensor performance: (a) RP15b; (b) RP25b.

The coprecipitated powders were exåmined using SEM after the immersion tests. Figure 6 shows typical SEM micrograph of the probe cross-section for RP25a powder. It is obvious that the oxide powder was partially sintered. Most of the particles in the reference powder remains separated, which is very important advantage for the chemically produced powders in the industrial applications. As observed in the industrial trials, tight contact between the solid electrolyte and the reference powder during measurements of the oxygen concentration ensures a stable reference potential, rapid electrochemical equilibrium and short response times [14].

CONCLUSION

Influence of the chemically coprecipitated reference powders on the performance of the oxygen sensors in the oxygen activity measurements has been investigated. The reference electrode powders produced by the oxide coprecipitation perform very well in terms of the EMF reproducibility and the response time for the low oxygen content measurements in the molten steel under industrial scale. The chemically produced Cr_2O_3–Fe_2O_3 powders very well adhere to the Cr particles. This fact gives good EMF reproducibility with a good Al relationship. An increase in Fe_2O_3 content of the oxide powder reduces the EMF overshoot and improves the trace quality. More positive EMF measurements, lower Al predictions than the chemical analysis and reduced probe accuracy at higher Al contents are obtained with decreasing the oxide content of the reference powder. In spite of the bath temperature in the molten steel, over 1600°C, the chemical production powders are partially sintered, which should lead to a much more attention on the method of the reference powder production used in this study.

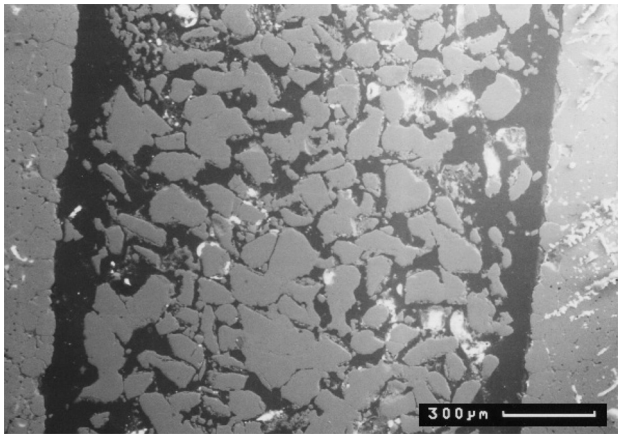


Figure 6. Typical SEM micrograph of the reference powders after immersion to the molten steel.

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VLIV CHARAKTERISTIK PRÁŠKU REFERENČNÍ ELEKTRODY NA FUNKČNOST ZIRKONIČITÝCH KYSLÍKOVÝCH SOND

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Prášek referenční elektrody je důležitou částí, která ovlivňuje funkčnost zirkoničitých kyslíkových sond. Nové referenční prášky s různým obsahem směsi Cr_2O_3–Fe_2O_3 a poměrem kov-oxid byly připraveny chemickou cestou spolusrážením. Mikrostrukturní analýza prášků byla provedena skenovací elektronovou mikroskopií. Funkčnost prášků byla testována měřením aktivity kyslíku v roztavených ocelích v ocelářské praxi. Prášky připravené srážením oxidů mají velmi dobrou EMF reprodukovatelnost a čas odezvy při měření nízkých koncentrací kyslíku. Směsné prášky Cr_2O_3–Fe_2O_3 velmi dobře přilnou k Cr částicím, což dává dobrou reprodukovatelnost odezvy a správnost stanoveného obsahu Al. Zvýšený obsah Fe_2O_3 redukuje EMF překmitnutí a zvyšuje přesnost měření. Nižší obsah oxidu v referenčním prášku přináší nižší stanovené obsahy hliníku v oceli ve srovnání s chemickou analýzou a snižuje správnost měření při vyšších obsazích Al.